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Isopiestic Determination of the Osmotic and Activity Coefficients of $\text{Li}_2\text{SO}_4(\text{aq})$ at $T = 298.15$ and 323.15 K, and Representation with an Extended Ion-interaction (Pitzer) Model

Joseph A. Rard · Simon L. Clegg · Donald A. Palmer

Abstract Isopiestic vapor-pressure measurements were made for $\text{Li}_2\text{SO}_4(\text{aq})$ from 0.1069 to $2.8190 \text{ mol}\cdot\text{kg}^{-1}$ at 298.15 K, and from 0.1148 to $2.7969 \text{ mol}\cdot\text{kg}^{-1}$ at 323.15 K, with $\text{NaCl}(\text{aq})$ as the reference standard. Published thermodynamic data for this system were reviewed, recalculated for consistency, and critically assessed. The present results and the more reliable published results were used to evaluate the parameters of an extended version of Pitzer's ion-interaction model with an ionic-strength dependent third virial coefficient, as well as those of the standard Pitzer model, for the osmotic and activity coefficients at both temperatures. Published enthalpies of dilution at 298.15 K were also analyzed to yield the parameters of the ion-interaction models for the relative apparent molar enthalpies of dilution. The resulting models at 298.15 K are valid to the saturated solution molality of the thermodynamically stable phase $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{cr})$. Solubilities of $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{cr})$ at 298.15 K were assessed, and the selected value of $m(\text{sat.}) = 3.13 \pm 0.04 \text{ mol}\cdot\text{kg}^{-1}$ was used to evaluate the thermodynamic solubility product $K_s(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (2.62 \pm 0.19)$ and a CODATA-compatible standard molar Gibbs energy of formation $\Delta_f G_m^\circ(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1564.6 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$.

Keywords Lithium sulfate · Aqueous solutions · Isopiestic measurements · Ion-interaction model · Pitzer model · Solubility product · Standard thermodynamic properties

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1. Introduction

Both Na_2SO_4 and K_2SO_4 occur widely in natural waters and are found in many evaporite deposits. Consequently, their thermodynamic properties have been widely studied and models are available that represent these thermodynamic properties over wide ranges of molality and temperature [1–3]. Thermodynamic data for the more rare alkali metal sulfates $\text{Rb}_2\text{SO}_4(\text{aq})$ and $\text{Cs}_2\text{SO}_4(\text{aq})$ are much less extensive. Isopiestic data are available only at 298.15 and 323.15 K for $\text{Rb}_2\text{SO}_4(\text{aq})$ and enthalpies of dilution are limited to 298.15 K and are incomplete [4]. The available thermodynamic data for $\text{Cs}_2\text{SO}_4(\text{aq})$ include isopiestic results at 298.15 and 323.15 K [4] and from 383.14 to 498.19 K [5]. However, the enthalpies of dilution for $\text{Cs}_2\text{SO}_4(\text{aq})$ are very limited in extent and quality and there is an absence of heat capacities. Thus the thermodynamic properties in the region between the high temperature and low temperature isopiestic measurements have not been characterized. A similar situation exists for $\text{Li}_2\text{SO}_4(\text{aq})$ where there is a gap between the low-temperature thermodynamic measurements, summarized in reference [3], and the high-temperature isopiestic measurements of Holmes and Mesmer [5].

Because of the incomplete characterization of the thermodynamic properties of most of the aqueous alkali metal sulfates at intermediate temperatures, an extensive series of isopiestic measurements was made at Oak Ridge National Laboratory between 1985 and 1997 at temperatures of 298.15 and 323.15 K. There were no isopiestic data available for the alkali metal sulfates at 323.15 K prior to these measurements. The results for $\text{Na}_2\text{SO}_4(\text{aq})$ [1], $\text{K}_2\text{SO}_4(\text{aq})$ [2], $\text{Rb}_2\text{SO}_4(\text{aq})$ and $\text{Cs}_2\text{SO}_4(\text{aq})$ [4] have already been published. In the present report new isopiestic data for $\text{Li}_2\text{SO}_4(\text{aq})$ are presented, published thermodynamic data are recalculated consistently and critically assessed, and the more reliable of these results are represented with Pitzer's ion-interaction model [6] and with an extended form that has an ionic-strength dependent C -term as described by Archer [7].

2. Experimental

The isopiestic experiments were performed at Oak Ridge National Laboratory (ORNL), at both $T = 298.15 \pm 0.00_3$ and $323.15 \pm 0.00_3$ K, using a slightly modified version of the apparatus described by Rush and Johnson [8]. This apparatus, its operation, the equilibration times, the water purification method, and the experimental conditions and techniques are essentially identical to those described in previous reports [1,2,4]. Rard and Platford [9] give a detailed description of the isopiestic method with an emphasis on experimental aspects and possible errors.

Eight different stock solutions of NaCl(aq) were used as the isopiestic reference standards. The same NaCl(aq) reference standard solutions were also used in the Cs₂SO₄(aq) experiments [4], and the preparations and molality analyses of these NaCl(aq) stock solutions are described in that report and reference [1]. The methods used to analyze the molalities of the seven Li₂SO₄(aq) stock solutions are identical to those described for the Na₂SO₄(aq) stock solutions [1]. Table 1 summarizes the molalities of the individual NaCl(aq) and Li₂SO₄(aq) stock solutions and the method of determination of the molalities. Assumed molar masses are 58.4428 g·mol⁻¹ for NaCl, 109.945 g·mol⁻¹ for Li₂SO₄, and 18.0153 g·mol⁻¹ for H₂O. All apparent masses were converted to masses using buoyancy corrections.

The various Li₂SO₄(aq) stock solutions were prepared from Li₂SO₄·H₂O(s) and water that was purified as described elsewhere [1]. Samples from three separate lots of Alfa Products (stated purity 99.8 %) and two lots of Aldrich Chemicals Gold Label (stated purity 99.999 %) Li₂SO₄·H₂O(s) were used for the solution preparations. The stock solutions with molalities of $m = 0.96408$ and 0.95864 mol·kg⁻¹ were prepared from Alfa

Products lot # 030982, stock solutions with $m = 0.96320$ and $0.97884 \text{ mol}\cdot\text{kg}^{-1}$ from Alfa Products lot # 011378, and the stock solution with $m = 0.17134 \text{ mol}\cdot\text{kg}^{-1}$ from lot # 030983. Aldrich Chemicals Gold Label lot # 2125DJ was used to prepare the stock solution with $m = 0.83846 \text{ mol}\cdot\text{kg}^{-1}$ and lot # 012084LP the $m = 1.0622 \text{ mol}\cdot\text{kg}^{-1}$ stock solution.

Natural sources of lithium are mixtures of ^6Li (with a molar mass of $6.015123 \text{ g}\cdot\text{mol}^{-1}$) and ^7Li (with a molar mass of $7.016005 \text{ g}\cdot\text{mol}^{-1}$), with ^7Li being the predominant isotope. The recommended molar mass of lithium from natural sources is $6.941 \text{ g}\cdot\text{mol}^{-1}$. However, many commercial sources of lithium salts are depleted in ^6Li (which is selectively removed for use in production of tritium) and have a lithium molar mass that ranges up to $6.99 \text{ g}\cdot\text{mol}^{-1}$. Thus, the molar mass of Li_2SO_4 can range between $109.945 \text{ g}\cdot\text{mol}^{-1}$ and $110.045 \text{ g}\cdot\text{mol}^{-1}$. Unfortunately, commercial samples of lithium salts usually do not list the lithium isotopic composition.

The number of moles of Li_2SO_4 in the analyzed samples of our stock solutions were determined either by gravimetric analysis by precipitation of the sulfate as $\text{BaSO}_4(\text{s})$, or by analysis of the amount of lithium using cation-exchange chromatography followed by mass titration of the eluted H^+ with $\text{NaOH}(\text{aq})$. Thus, the determined number of moles of Li_2SO_4 does not depend on an assumed molar mass for Li. However, the mass fraction of H_2O in each of these samples, which was calculated as the difference between the measured solution mass and the calculated mass of anhydrous Li_2SO_4 , does depend on the assumed molar mass of Li_2SO_4 . The resulting uncertainties in the reported isopiestic molalities in Tables 2 and 3 are negligible at the lowest concentrations of $\approx 0.1 \text{ mol}\cdot\text{kg}^{-1}$, but increase with increasing molality to 0.028 % at $\approx 2.8 \text{ mol}\cdot\text{kg}^{-1}$ (the highest studied molalities). This 0.028 % uncertainty is smaller than the typical uncertainties resulting from the isopiestic equilibrations.

The molality-based osmotic coefficients ϕ of $\text{Li}_2\text{SO}_4(\text{aq})$ were calculated using the fundamental equation for isopiestic equilibrium:

$$\phi = \nu^* m^* \phi^* / \nu m \quad (1)$$

where $\nu = 3$ is the stoichiometric ionization number and m the molality of $\text{Li}_2\text{SO}_4(\text{aq})$, and the corresponding quantities for the reference standard solution at isopiestic equilibrium are denoted with an asterisk. The osmotic coefficients of the $\text{NaCl}(\text{aq})$ reference standard solution at the experimental molalities and temperatures were calculated with the equation and parameters of Archer [7]. The experimental isopiestic molalities and calculated osmotic coefficients at 298.15 K are reported in Table 2 and at 323.15 K in Table 3.

The experiments of most of the series involved measurements at a single temperature, but those of Series 4, 8, 10, and 13 included experiments at both 298.15 and 323.15 K. The ratio $m(\text{Li}_2\text{SO}_4)/m(\text{NaCl})$ at isopiestic equilibrium varies significantly with both concentration and temperature. The rather large uncertainties of the molalities of the first experiment each of Series 4 and 13 at 298.15 K are probably the result of the 25 K temperature change that occurred from the previous equilibration, without allowing sufficient extra time to reattain isopiestic equilibrium.

A graphical comparison was made of the osmotic coefficients of $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 K from Table 2 and at 323.15 from Table 3. This comparison indicates that the values of ϕ from Series 4 at both temperatures and the first experiment of Series 13 at 298.15 K are significantly lower than those from the other series of experiments ($\Delta\phi \approx -0.01$ to -0.03), and the two ϕ values from Series 12 at 323.15 K are considerably lower ($\Delta\phi \approx -0.1$). These values of ϕ were rejected as being erroneous. We note that $\text{Na}_2\text{SO}_4(\text{aq})$, $\text{Rb}_2\text{SO}_4(\text{aq})$, and $\text{Cs}_2\text{SO}_4(\text{aq})$ samples were also present for the Series 4 experiments and many of their osmotic coefficients were also rejected as being low [1,4], which suggests that there may

have been an error in the molality of the NaCl(aq) stock solution used as a reference standard for Series 4. The remaining experiments at 323.15 K (Series 8, 9, 9A, 10, 11, and 13) are consistent, as are most of the series of experiments at 298.15 K (Series 3, 5, 6, 7, 8, and 10). Osmotic coefficients from Series 1 and 2 at 298.15 K are consistent with each other but are higher ($\Delta\phi \approx +0.006$ to $+0.01$) than those from the six consistent series. Because Series 1 and 2 involved the same NaCl(aq) and Li₂SO₄(aq) stock solutions, it is possible that the molality of one of these stock solutions is slightly in error.

3. Analysis of published thermodynamic data for Li₂SO₄(aq)

There are several previous studies that reported isopiestic data for Li₂SO₄(aq) at 298.15 K. Robinson *et al.* [10] reported results from 0.07310 to 3.165 mol·kg⁻¹ (near saturation) with KCl(aq) as reference standard. Michimoto *et al.* [11] reported isopiestic measurements with H₂SO₄(aq) as reference standard but did not list the equilibration molalities; however, these molalities (0.4938 to 1.8204 mol·kg⁻¹) were later given by Majima *et al.* [12]. Filippov and Kalinkin [13] reported four osmotic coefficients from 0.952 to 2.875 mol·kg⁻¹ but did not give the molalities of the reference standard. Filippov *et al.* [14,15] reported isopiestic results from 0.6996 to 3.0403 mol·kg⁻¹ with NaCl(aq) as reference solution; these studies include the detailed results for the four equilibrations reported by Filippov and Kalinkin [13] but give the equilibrium molalities to an additional significant figure. The isopiestic molality of Li₂SO₄(aq) in equilibrium with a NaCl(aq) solution of molality 3.7924 mol·kg⁻¹ is given as $m(\text{Li}_2\text{SO}_4) = 2.8764 \text{ mol}\cdot\text{kg}^{-1}$ in reference [14] and as $m(\text{Li}_2\text{SO}_4) = 2.8746 \text{ mol}\cdot\text{kg}^{-1}$ in reference [15], with the last two digits transposed. By comparison with the results reported in reference [13], $m(\text{Li}_2\text{SO}_4) = 2.8746 \text{ mol}\cdot\text{kg}^{-1}$ appears to be the correct molality. Baabor *et al.* [16] reported isopiestic data for the Li₂SO₄ + Na₂SO₄ + H₂O system at 298.15 K, including the limiting binary

solutions, which could be used to calculate another set of osmotic coefficients for $\text{Li}_2\text{SO}_4(\text{aq})$ from 0.07350 to 2.6690 $\text{mol}\cdot\text{kg}^{-1}$ if $\text{Na}_2\text{SO}_4(\text{aq})$ were used as a provisional reference electrolyte. Baabor *et al.* [17] also reported isopiestic results for $\text{Li}_2\text{SO}_4(\text{aq})$ from 0.0802 to 2.5658 $\text{mol}\cdot\text{kg}^{-1}$ at 313.15 K and Holmes and Mesmer [5] reported isopiestic results from 383.14 to 498.19 K ranging up to 2.4 to 3.2 $\text{mol}\cdot\text{kg}^{-1}$ (depending on the temperature); both of these studies used $\text{NaCl}(\text{aq})$ as the reference standard.

Filippov and Kalinkin [13] also reported that the water activity and molality of a saturated solution at 298.15 K were $a_w = 0.846$ and $m(\text{sat.}) = 3.123 \text{ mol}\cdot\text{kg}^{-1}$, respectively, which yields an osmotic coefficient of $\phi(\text{sat.}) = 0.990_8$.

The osmotic coefficients of $\text{Li}_2\text{SO}_4(\text{aq})$ from isopiestic measurements at 298.15 K [10–12,14,15] were recalculated for consistency using current critical evaluations of the thermodynamic properties of the reference standards $\text{NaCl}(\text{aq})$ [7], $\text{KCl}(\text{aq})$ [18], and $\text{H}_2\text{SO}_4(\text{aq})$ [19].

Direct measurements of the vapor pressures of $\text{Li}_2\text{SO}_4(\text{aq})$ solutions of known molality have been reported by Pearce and Eckstrom [20] from 0.1 to 3.0944 $\text{mol}\cdot\text{kg}^{-1}$ at 298.15 K, by Kangro and Groeneveld [21] from 0.5 to 3.0 $\text{mol}\cdot\text{kg}^{-1}$ at 293.15 and 298.15 K, and by Abdulagatov and Azizov [22] at molalities of 0.279, 0.886, 1.322, and 1.600 $\text{mol}\cdot\text{kg}^{-1}$ and temperatures of 423.15 to 573.15 K (these last authors also cited other high-temperature vapor pressure studies). Osmotic coefficients were calculated from the reported vapor pressures of the first two of these studies [20,21] by using Eq. (26) of Rard and Platford [9]. The vapor pressures of Abdulagatov and Azizov [22] were not reanalyzed because they are well above the temperature range being modeled. However, based on the comparison of results from various studies presented in their Figs. 9 and 10, there are large discrepancies among these high-temperature studies.

El Guendouzi *et al.* [23] reported water activities and osmotic coefficients for $\text{Li}_2\text{SO}_4(\text{aq})$ from 0.1 to 3.0 $\text{mol}\cdot\text{kg}^{-1}$ at 298.15 K from measurements by their hygrometric method. They estimated the uncertainties of their osmotic coefficients as being “at most, ± 0.006 ”. This imprecision is significantly larger than that usually obtained in isopiestic experiments.

There are several published studies of the vapor pressures of saturated solutions of $\text{Li}_2\text{SO}_4(\text{aq})$. To calculate osmotic coefficients from these vapor pressures requires values of the saturated solution molalities at the experimental temperatures that are taken or interpolated from published sources rather than being measured, which could result in large discrepancies because of uncertainties in the saturated solution molalities (see below, Section 5). Applebey *et al.* [24] reported vapor pressures of saturated solutions from 298.45 to 373.50 K, Rockland [25] from 278.15 to 313.15 K, and Apleblat and Korin [26] from 282.15 to 322.25 K. The results of Rockland, which were reported as percent relative humidity to only two significant figures, yield $\phi(\text{sat.}) = 0.96$ using the selected saturated solution molality of $m(\text{sat.}) = 3.131 \text{ mol}\cdot\text{kg}^{-1}$ (see below). Because of the low precision of the reported relative humidity measurements, this result was not considered further, but the osmotic coefficient agrees with the more consistent isopiestic results to $\Delta\phi = -0.04$.

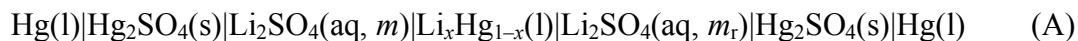
A preliminary comparison was made of the osmotic coefficients at 298.15 K derived from isopiestic and direct vapor pressure measurements. Most of the osmotic coefficients from isopiestic studies [10,14,15], including the present results from Table 2 (excluding a few measurements as described above), are generally in good agreement. Osmotic coefficients from the isopiestic study of Majima *et al.* [11,12] agree with the more consistent isopiestic results to within $\Delta\phi = \pm 0.01$ except at the two highest molalities

where they are 0.015 to 0.03 lower; because of the low precision, these results were rejected.

The hygrometric results of El Guendouzi *et al.* [23] are in general agreement with the isopiestic results but are more scattered, with most of their values falling within the $\Delta\phi = \pm 0.006$ uncertainty claimed by the authors (with one point being low by $\Delta\phi \approx -0.009$), and Kangro and Groeneveld's [21] vapor results are consistently lower by $\Delta\phi \approx -0.01$. Most of the osmotic coefficients calculated from the vapor pressures of Pearce and Eckstrom [20] are within ≈ 0.02 of the isopiestic and hygrometric results up to 1.5 mol·kg⁻¹ (and are generally lower), but then show increasing significant molality-dependent systematic deviations of $\Delta\phi \approx -0.04$ to ≈ -0.08 . The osmotic coefficient of the saturated solution reported by Apelblat and Korin [26] at 298.15 K (based on their interpolation of their vapor pressures to this temperature), $\phi(\text{sat.}) = 1.174$, is too high by $\Delta\phi \approx 0.17$ (17%). None of the osmotic coefficients from the studies discussed in this paragraph were included in the Archer and Pitzer model fits, described below, because of their low precision or systematic errors.

Freezing temperature depressions for Li₂SO₄(aq) from 0.00704 to 1.0139 mol·kg⁻¹ have been reported by Indelli [27] that could be used to calculate osmotic coefficients at the freezing temperatures of the solutions. However, because of the lack of reliable heat capacities, it was not possible to make an accurate conversion of these results to osmotic coefficients at 298.15 K.

Åkerlöf [28] reported Emfs for the following concentration cell without transport at 298.15 K:

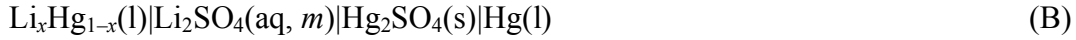


For this cell the Emf is given by:

$$\begin{aligned}
E(\text{cell A}) &= (RT/2F)\ln\{a(\text{Li}_2\text{SO}_4)/\{a_r(\text{Li}_2\text{SO}_4)\}\} \\
&= (3RT/2F)\ln(m\gamma_{\pm}/m_r\gamma_{\pm,r})
\end{aligned} \tag{2}$$

where m is the solution molality, $a(\text{Li}_2\text{SO}_4)$ is the thermodynamic activity of $\text{Li}_2\text{SO}_4(\text{aq})$, γ_{\pm} is the mean (molality-based) activity coefficient of $\text{Li}_2\text{SO}_4(\text{aq})$, and the corresponding quantities at the reference molality ($m_r = 0.05 \text{ mol}\cdot\text{kg}^{-1}$) are denoted with a subscripted r . Both molarity and molality concentrations were reported in this study. As noted by Rard *et al.* [1], the reported molalities are smaller than the molarities whereas they should be larger, and we assume that the two sets of concentrations should be reversed.

Faverio *et al.* [29] reported Emfs at 298.15 K for the following electrochemical cell with a flowing lithium amalgam:

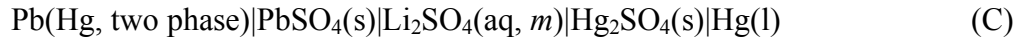


where $x = 0.00493$ is the mole fraction of Li in the amalgam. The Emf is given by

$$\begin{aligned}
E(\text{cell B}) &= E^\circ(\text{cell B}) - (RT/2F)\ln\{a(\text{Li}_2\text{SO}_4)\} \\
&= E^\circ(\text{cell B}) - (3RT/2F)\ln\{4^{1/3}(m/\text{mol}\cdot\text{kg}^{-1})\gamma_{\pm}\}
\end{aligned} \tag{3}$$

and the molalities range from 0.05 to $2.9 \text{ mol}\cdot\text{kg}^{-1}$.

Fusi and Mussini [30] reported Emfs at 298.15 K for the following cell:



The Emf of this cell is independent of the molality and thus does not yield thermodynamic data for $\text{Li}_2\text{SO}_4(\text{aq})$. These measurements were used by the authors as part of their assessment of the reliability of the $\text{Pb}(\text{Hg, two phase})|\text{PbSO}_4(\text{s})$ electrode.

As described by Åkerlöf [28], the $\text{Li}_x\text{Hg}_{1-x}(\text{l})$ electrode is subject to oxidation of Li by $\text{H}^+(\text{aq})$ if the solution is acidic, whereas the $\text{Hg}_2\text{SO}_4(\text{s})$ electrode can become contaminated with a $\text{Hg}(\text{I})$ hydroxysulfate if the solution pH is neutral or alkaline. Both of these effects can affect the measured Emfs. The second problem has been discussed in

more detail by Rard and Clegg [33] who also noted that formation of the yellow hydroxysulfate could be suppressed by protecting the electrode system from exposure to light.

Mussini *et al.* [31] reported Emfs for $\text{Li}_2\text{SO}_4(\text{aq})$ solutions from 0.1 to 3.0 $\text{mol}\cdot\text{kg}^{-1}$ at 298.15 K for a concentration cell with transport, which was used by the authors to derive the transference number of the Li^+ ion. Sircar *et al.* [32] reported similar results at 308.15 K. If highly reliable transference numbers were to become available from some independent method, then these Emfs could be used to derive relative activity coefficients for $\text{Li}_2\text{SO}_4(\text{aq})$.

The molar enthalpies of dilution of $\text{Li}_2\text{SO}_4(\text{aq})$, $\Delta_{\text{dil}}H_{\text{m}}$, have been reported in several studies. The enthalpies of dilution are related to the relative apparent molar enthalpies L_{ϕ} by:

$$\Delta_{\text{dil}}H_{\text{m}} = L_{\phi}(m_{\text{f}}) - L_{\phi}(m_{\text{i}}) \quad (4)$$

where m_{i} is the initial molality before mixing with water and m_{f} is the final molality after dilution. Enthalpies of dilution at 298.15 K have been reported at 298.15 K by Lange and Streeck [34] from 1.645×10^{-4} to 0.1 $\text{mol}\cdot\text{L}^{-1}$, by Thompson *et al.* [35] from 0.0914 to 3.00 $\text{mol}\cdot\text{kg}^{-1}$, by Solov'eva *et al.* [36] from 0.278 to 3.08 $\text{mol}\cdot\text{kg}^{-1}$, and by Frolov *et al.* [37] from 0.05 to 2.99 $\text{mol}\cdot\text{kg}^{-1}$. Frolov *et al.* also reported enthalpies of dilution from 0.08 to 3.00 $\text{mol}\cdot\text{kg}^{-1}$ at 283.15 K and from 0.20 to 2.99 $\text{mol}\cdot\text{kg}^{-1}$ at 313.15 K. Leung and Millero [38] reported enthalpies of dilution from 0.17278 to 0.91859 $\text{mol}\cdot\text{kg}^{-1}$ at 303.15 K. The concentrations reported by Lange and Streeck [34] were converted to molalities using the densities reported by Pearce and Eckstrom [20].

Apelblat [39] reported enthalpies of solution at 298.15 K of the thermodynamically stable phase $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{s})$ (corrected for a slight water excess), along with those of the

anhydrous phase $\text{Li}_2\text{SO}_4(\text{s})$. Apelblat's standard enthalpy of solution of $\text{Li}_2\text{SO}_4(\text{cr})$ at infinite dilution, $\Delta_{\text{sol}} H_{\text{m}}^{\infty}(\text{Li}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = -(30.502 \pm 0.170) \text{ kJ}\cdot\text{mol}^{-1}$, is in complete agreement with the NIST-JANAF assessment [40], $\Delta_{\text{sol}} H_{\text{m}}^{\infty}(\text{Li}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = -(30.5 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$, which is based on older literature data.

Apelblat [39] also reported heat capacities c_p of 0.06233 to 0.9409 $\text{mol}\cdot\text{kg}^{-1}$ $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 K. These values of c_p were first normalized to the heat capacity of water calculated from Hill's equation of state [41] and then converted to the apparent molar heat capacities $C_{p,\phi}$ of Li_2SO_4 in the solutions using the relation:

$$C_{p,\phi} = M c_p + \left\{ \frac{c_p - c_{p,1}}{m} \right\} \quad (5)$$

where $M = 109.945 \text{ g}\cdot\text{mol}^{-1}$ is the molar mass of Li_2SO_4 and $c_{p,1}$ is the heat capacity per gram of the solvent (H_2O). Apelblat [39] stated that these heat capacities were: “not accurate enough to calculate $C_{p,m,\phi}$ values especially for molalities less than $m = 0.2 \text{ mol}\cdot\text{kg}^{-1}$ ”. The calculated values of $C_{p,\phi}$ at the two lowest molalities appear to be too negative by about $150 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and those from $m = 0.2811$ to $0.9409 \text{ mol}\cdot\text{kg}^{-1}$ are scattered by about $40 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Because of their low accuracy and precision, these results were not considered further.

Table 4 summarizes the results from these studies reporting thermodynamic data for $\text{Li}_2\text{SO}_4(\text{aq})$ including the type of measurement, molality range and temperature(s) studied, and number of data points.

4. Formation of LiSO_4^- ion-pairs in $\text{Li}_2\text{SO}_4(\text{aq})$ solutions

There are several studies that report equilibrium constants for the following reaction:



Reardon [42] reported results that yield an association constant $K_a(\text{LiSO}_4^-) = 5.9 \pm 0.7$ derived from activity coefficients and cited a literature value of $K_a(\text{LiSO}_4^-) = 4.4$ from electrical conductance measurements, and Fisher and Fox [43] reported results that give $K_a(\text{LiSO}_4^-) = 10.4 \pm 0.5$ from electrical conductance measurements, all at 298.15 K. Daniele *et al.* [44] reported results that yield $K(\text{LiSO}_4^-) = 13.2$ at 310.15 K from potentiometric measurements. All of these values are fairly uncertain because of the sensitivity of the derived results to the approximate methods used estimate ionic activity coefficients. However, it was previously found for the other alkali metal sulfates that the effect of these weak ion-pairs can be neglected when analyzing the thermodynamic properties with Pitzer's ion-interaction model [1,2,4,6], and thus the presence of these ion-pairs will also be neglected for $\text{Li}_2\text{SO}_4(\text{aq})$.

5. Results and evaluation of the ion-interaction model parameters

We represented the available thermodynamic data for $\text{Li}_2\text{SO}_4(\text{aq})$ using an extended form of Pitzer's ion-interaction model [6] that was described by Archer [7]. For the molality-based osmotic coefficient of $\text{Li}_2\text{SO}_4(\text{aq})$, the model equation has the form:

$$\phi - 1 = -2A_\phi I^{1/2}/(1 + bI^{1/2}) + (4/3)mB^\phi(\text{Li},\text{SO}_4) + (16/3)m^2C^{\text{T}\phi}(\text{Li},\text{SO}_4) \quad (7)$$

where m is the stoichiometric molality, $I = 3m$ is the ionic strength, $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$, and A_ϕ is the Debye-Hückel limiting-law slope for the osmotic coefficient. The ionic-strength dependent functions $B^\phi(\text{Li},\text{SO}_4)$ and $C^{\text{T}\phi}(\text{Li},\text{SO}_4)$ are defined by:

$$B^\phi(\text{Li}, \text{SO}_4) = \beta^{(0)}(\text{Li}, \text{SO}_4) + \beta^{(1)}(\text{Li}, \text{SO}_4) \cdot \exp(-\alpha I^{1/2}) \quad (8)$$

and

$$C^{\text{T}\phi}(\text{Li}, \text{SO}_4) = C^{(0)}(\text{Li}, \text{SO}_4) + C^{(1)}(\text{Li}, \text{SO}_4) \cdot \exp(-\omega I^{1/2}) \quad (9)$$

The value of the first exponential coefficient is generally fixed at $\alpha = 2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ [6], although smaller values have been used previously for the alkali metal sulfates [5].

The corresponding expression for the natural logarithm of the mean activity coefficient γ_{\pm} of $\text{Li}_2\text{SO}_4(\text{aq})$ is:

$$\begin{aligned} \ln \gamma_{\pm} = & -2A_\phi \{ I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2}) \} + (4/3)m[2\beta^{(0)}(\text{Li}, \text{SO}_4) \\ & + 2\{\beta^{(1)}(\text{Li}, \text{SO}_4)/\alpha^2 I\} \{1 - (1 + \alpha I^{1/2} - \alpha^2 I/2)\exp(-\alpha I^{1/2})\}] \\ & + (8/3)m^2[3C^{(0)}(\text{Li}, \text{SO}_4) + \{4C^{(1)}(\text{Li}, \text{SO}_4)/(\omega^4 I^2)\} \{6 - (6 + 6\omega I^{1/2} + 3\omega^2 I + \omega^3 I^{3/2}) \\ & - \omega^4 I^2/2)\exp(-\omega I^{1/2})\}] \end{aligned} \quad (10)$$

The expressions for the relative apparent molar enthalpy and apparent molar heat capacity are, respectively:

$$L_\phi = (6A_H/2b)\ln(1 + bI^{1/2}) - 4RT^2\{mB^L(\text{Li}, \text{SO}_4) + 2m^2C^L(\text{Li}, \text{SO}_4)\} \quad (11)$$

$$C_{p,\phi} = C_{p,\phi}^\circ + (6A_C/2b)\ln(1 + bI^{1/2}) - 4RT^2\{mB^C(\text{Li}, \text{SO}_4) + 2m^2C^C(\text{Li}, \text{SO}_4)\} \quad (12)$$

where $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is the gas constant, T is the absolute temperature, and where:

$$B^L(\text{Li}, \text{SO}_4) = \left\{ \frac{\partial \beta^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p + 2 \left\{ \frac{\partial \beta^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p \{1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\}/(\alpha^2 I) \quad (13)$$

$$C^L(\text{Li}, \text{SO}_4) = \left\{ \frac{\partial C^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p + 4 \left\{ \frac{\partial C^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p \{6 - (6 + 6\omega I^{1/2} + 3\omega^2 I + \omega^3 I^{3/2})\exp(-\omega I^{1/2})\}/(\omega^4 I^2) \quad (14)$$

$$B^C(\text{Li}, \text{SO}_4) = \left\{ \frac{\partial^2 \beta^{(0)}(\text{Li}, \text{SO}_4)}{\partial T^2} \right\}_p + (2/T) \left\{ \frac{\partial \beta^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p + 2 \left[\left\{ \frac{\partial^2 \beta^{(1)}(\text{Li}, \text{SO}_4)}{\partial T^2} \right\}_p \right. \\ \left. + (2/T) \left\{ \frac{\partial \beta^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p \right] \left[\{1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})\} \right] / (\alpha^2 I) \quad (15)$$

$$C^C(\text{Li}, \text{SO}_4) = \left\{ \frac{\partial^2 C^{(0)}(\text{Li}, \text{SO}_4)}{\partial T^2} \right\}_p + (2/T) \left\{ \frac{\partial C^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p + 4 \left[\left\{ \frac{\partial^2 C^{(1)}(\text{Li}, \text{SO}_4)}{\partial T^2} \right\}_p \right. \\ \left. + (2/T) \left\{ \frac{\partial C^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p \right] \left[\{6 - (6 + 6\omega I^{1/2} + 3\omega^2 I + \omega^3 I^{3/2}) \exp(-\omega I^{1/2})\} \right] / (\omega^4 I^2) \quad (16)$$

In these equations A_H and A_C are the Debye-Hückel limiting law slopes for enthalpy and heat capacity, respectively. Values of A_ϕ , A_H , and A_C for water were calculated with the Chebychev polynomial given by Clegg *et al.* in their Appendix II [19] that is based on Archer and Wang's [45] evaluation of the Debye-Hückel limiting law slopes.

Because of the lack of reliable heat capacities for $\text{Li}_2\text{SO}_4(\text{aq})$, it was not possible to evaluate the second temperature derivatives of the ion-interaction model parameters, *i.e.*, those for Eqs. (12), (15), and (16). In principle, if values of L_ϕ are available at more than one temperature, then they could be used to derive approximate values of $C_{p,\phi}$. Although enthalpies of dilution $\Delta_{\text{dil}}H_m$ are available at 283.15 and 313.15 K to high molalities [37], and at 303.15 K to moderate molalities [38], they must be extrapolated to infinite dilution to yield L_ϕ . However, the final dilution molalities of these studies do not extend below 0.08 to 0.20 mol·kg⁻¹, and comparison of the more extensive results at 298.15 K [34–37] indicates that the corrections to infinite dilution will be around 2 to 3 kJ·mol⁻¹. This exceeds the size of many of the measured $\Delta_{\text{dil}}H_m$ values, and thus the extrapolations to infinite dilution could yield large uncertainties in L_ϕ . In addition, the most extensive enthalpies of dilution are from the study of Frolov *et al.* [37], and our comparison of their results at 298.15 to those of three other studies [34–36] indicates that the data of Frolov *et*

al. are less reliable. Consequently, our model fits were restricted to 298.15 K (osmotic coefficients and enthalpies of dilution) and 323.15 K (osmotic coefficients).

For the evaluation of the model parameters of Eqs. (7) through (10) at 298.15 K, equal weights were given to the present isopiestic results reported in Tables 2, of Robinson *et al.* [10] and of Filippov *et al.* [14,15], except for a few outliers as described in Tables 2 and 4. Figure 1(a) shows these osmotic coefficients as a function of the square root of molality and Fig. 1(b) the deviations of the experimental osmotic coefficients from the extended ion-interaction (Archer) model for $\text{Li}_2\text{SO}_4(\text{aq})$ with the evaluated parameters reported in Table 5. It can be seen from Fig. 1(b) that the values of ϕ from these four studies are in very good agreement above $1 \text{ mol}\cdot\text{kg}^{-1}$, but the variations among them become slightly larger at lower molalities where ϕ becomes very sensitive to very small differences in the water activity. For example, an uncertainty of $\Delta\phi = \pm 0.005$ corresponds to an uncertainty of the water activity of $\Delta a_w = \pm 0.00048$ at $m = 2.0 \text{ mol}\cdot\text{kg}^{-1}$, $\Delta a_w = \pm 0.00013$ at $m = 0.5 \text{ mol}\cdot\text{kg}^{-1}$, but is only $\Delta a_w = \pm 0.00003$ at $m = 0.1 \text{ mol}\cdot\text{kg}^{-1}$.

Figure 2 shows the deviations of the $\text{Li}_2\text{SO}_4(\text{aq})$ osmotic coefficients at 298.15 K for non-isopiestic measurements of the vapor pressure [20,21,23,25]. These osmotic coefficients were not included in the model fits for reasons discussed in Section 3. Of these studies, the hygrometric results of El Guendouzi *et al.* [23] agree best with the isopiestic data.

Figure 3(a) shows our osmotic coefficients at 323.15 K from Table 3 as a function of the square root of molality and Fig. 3(b) the deviations of these experimental osmotic from the extended ion-interaction model whose parameters are reported in Table 5.

In Fig. 4 we shown the deviations of the Emfs for cells (A) and (B) at 298.15 K from values calculated with the ion-interaction model parameters of Table 5. Although these

Emfs were not used in the evaluation of the model parameters, the Emfs of Åkerlöf [28] are clearly consistent with our model within their large scatter. The Emfs of Faverio *et al.* [29] are more precise than those of Åkerlöf but show a slight systematic trend with molality. The model parameters of Table 5 were used with all of the reported Emfs of Faverio *et al.* to yield $E^\circ = 2.66960 \pm 0.00057$ V for cell B.

Figure 5(a) shows the relative apparent molar enthalpies L_ϕ of $\text{Li}_2\text{SO}_4(\text{aq})$ as a function of the square root of the initial molality, where the values for the final molality were calculated from the optimized extended ion-interaction model whose parameters are reported in Table 5, and Fig. 5(b) shows the deviations of the experimental enthalpies of dilution from the extended ion-interaction (Archer) model.

Table 6 reports smoothed values of ϕ , a_w , and γ_\pm of $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 and 323.15 K, and L_ϕ at 298.15 K that were calculated using the parameters of the extended ion-interaction model reported Table 5. A comparison of our values of ϕ to those of Robinson and Stokes [50] at 298.15 K shows good agreement with $\Delta\phi \leq 0.004$ for $m = 0.2$ to 3.0 $\text{mol}\cdot\text{kg}^{-1}$, which is consistent with the differences in source data used and the revision in the osmotic coefficients of the $\text{KCl}(\text{aq})$ reference standard used for this earlier evaluation. Larger differences are observed from the more recent evaluation of Goldberg [51] at low molalities, which probably resulted from a mismatch between the isopiestic data and freezing temperature results used in his model. Because of the lack of heat capacities for $\text{Li}_2\text{SO}_4(\text{aq})$, Goldberg assumed that they were equal to those of $\text{Na}_2\text{SO}_4(\text{aq})$, which may have introduced significant inaccuracies when converting freezing temperature depressions to osmotic coefficients at 298.15 K.

Parameters for the standard 3-parameter form of Pitzer's model [6] were also evaluated for $\text{Li}_2\text{SO}_4(\text{aq})$ and are reported in the footnote to Table 5. The $C(\text{Li},\text{SO}_4)$ parameters of

this model is defined by Eq. (53) of his review article [6]. Based on comparison of the standard deviations for the fits, the extended 4-parameter model gives a more accurate representation of the input data than the 3-parameter model, which is expected because of the different number of model parameters.

6. Evaluation of the thermodynamic solubility product and standard thermodynamic properties of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}(\text{cr})$

A value of the standard Gibbs energy of solution of the thermodynamically-stable phase $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}(\text{cr})$, $\Delta_{\text{sol}} G_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$, can be calculated from the mean activity coefficient $\gamma_{\pm}(\text{sat.})$ of $\text{Li}_2\text{SO}_4(\text{aq})$ at the saturated solution molality, $m(\text{sat.})$, and the water activity $a_{\text{w}}(\text{sat.})$ using the following equation:

$$\begin{aligned} \Delta_{\text{sol}} G_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) &= -RT \ln K_{\text{s}} \\ &= -RT \ln [4 \{ (m(\text{sat.}) / \text{mol} \cdot \text{kg}^{-1}) \}^3 \{ \gamma_{\pm} \}^3 a_{\text{w}}(\text{sat.})] \quad (17) \end{aligned}$$

Values of the thermodynamic solubility product, $K_{\text{s}} = 4 \{ (m(\text{sat.}) / \text{mol} \cdot \text{kg}^{-1}) \}^3 \{ \gamma_{\pm} \}^3 a_{\text{w}}(\text{sat.})$, and $\Delta_{\text{sol}} G_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$ can be calculated from the parameters of the extended ion-interaction model reported in Table 5 once the saturated solution molality $m(\text{sat.})$ has been evaluated.

Reported saturated solution molalities at 298.15 K are $m(\text{sat.}) = 3.0944 \text{ mol} \cdot \text{kg}^{-1}$ [20] and $m(\text{sat.}) = 3.123 \text{ mol} \cdot \text{kg}^{-1}$ [13]. Solubilities reported in other studies as mass-% of anhydrous solid were converted to molalities assuming a molar mass of $109.945 \text{ g} \cdot \text{mol}^{-1}$ for Li_2SO_4 . Linke [46] tabulated results from three older studies that yield $m(\text{sat.}) = 3.113$, 3.161 , and $3.144 \text{ mol} \cdot \text{kg}^{-1}$, Khripin's [47] results yield $m(\text{sat.}) = 3.087 \text{ mol} \cdot \text{kg}^{-1}$, and Shevchuk and Ushakov's results [48] yield $m(\text{sat.}) = 3.112 \text{ mol} \cdot \text{kg}^{-1}$. There is a fairly large variation among these values: $\Delta m(\text{sat.}) = 0.074 \text{ mol} \cdot \text{kg}^{-1}$ (2.4 %). This variation is

much larger than that expected from uncertainties in the analysis of the saturation solution molality, which is typically done gravimetrically by precipitation of the sulfate as $\text{BaSO}_4(\text{s})$ or by dehydration to form anhydrous $\text{Li}_2\text{SO}_4(\text{s})$.

Solubility experiments are typically performed by dissolving the solid phase in water or “saturation from below”, which could result in slightly low apparent saturation molalities if insufficient time were allowed for the solution plus solid phase to reach thermodynamic equilibrium. We thus assume that the two lowest saturation molalities [20,47] are erroneously low, and averaged the remaining five values to yield the recommended result of $m(\text{sat.}) = 3.131 \pm 0.042 \text{ mol}\cdot\text{kg}^{-1}$, where the assigned uncertainty is the 95-% confidence limit. The water activity at this saturation molality, $a_{\text{w}}(\text{sat.}) = 0.84405 \pm 0.00084$, was calculated with the parameters of Table 5, where the 95-% confidence limit uncertainty is based on the standard error for the osmotic coefficient fit multiplied by 1.96. Similarly, the activity coefficient of the saturated solution, assuming a 2 % uncertainty, is $\gamma_{\pm}(\text{sat.}) = 0.2954 \pm 0.0059$. Combining these results, and using Eq. (17), yields $K_{\text{s}} = 2.617 \pm 0.193$ and $\Delta_{\text{sol}}G_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(2.385 \pm 0.183) \text{ kJ}\cdot\text{mol}^{-1}$.

Apelblat [39] reported fourteen enthalpies of solution for Merck Suprapure $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{cr})$ and eight for Alfa Inorganics Ultrapure $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{cr})$. Extrapolating these results to infinite dilution using the extended ion-interaction model parameters of Table 5 yields values of $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(17.830 \pm 0.155) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(17.907 \pm 0.149) \text{ kJ}\cdot\text{mol}^{-1}$, respectively, where the uncertainties are the 95-% confidence limits. Our recommended value is the average of these two results weighted by the number of measurements: $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(17.86 \pm 0.15) \text{ kJ}\cdot\text{mol}^{-1}$. Combining this result with the value of $\Delta_{\text{sol}}G_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$ given

in the preceding paragraph then yields $\Delta_{\text{sol}} S_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(51.90 \pm 0.80) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

Combining these results with the CODATA [49] recommended values for the standard thermodynamic properties of $\text{Li}^+(\text{aq})$, $\text{SO}_4^{2-}(\text{aq})$, and $\text{H}_2\text{O}(\text{l})$ yields $\Delta_{\text{f}} G_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1564.60 \pm 0.51) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1734.25 \pm 0.46) \text{ kJ} \cdot \text{mol}^{-1}$, and $S_{\text{m}}^{\circ}(\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (164.83 \pm 0.94) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. These results are in good agreement with those reported in the NBS tables [52].

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Table 1 Molalities of the NaCl(aq) and Li₂SO₄(aq) stock solutions

Series	$m(\text{NaCl})/$ $\text{mol}\cdot\text{kg}^{-1}$	$m(\text{NaCl})/$ $\text{mol}\cdot\text{kg}^{-1}$	$m(\text{Li}_2\text{SO}_4)/$ $\text{mol}\cdot\text{kg}^{-1}$	$m(\text{Li}_2\text{SO}_4)/$ $\text{mol}\cdot\text{kg}^{-1}$
1,2	0.9748 ^a		0.96408 ^b	
3	0.9852 ^a		0.95864 ^{b,d}	
4	1.0922 ^a		0.83846 ^c	
5	0.9868 ^a	1.1228 ^a	0.96320 ^c	
6	0.9868 ^a		0.96320 ^c	
7	1.1228 ^a		0.96320 ^c	
8, 11, 12	0.19580 ^a		0.17134 ^c	
9, 10	0.9869 ^a		0.96320 ^c	
13	0.91218 ^a		1.0622 ^c	0.97884 ^c

^a The source of the NaCl samples and methods of determining the molalities of these NaCl(aq) stock solutions were reported previously [1,4].

^b These two Li₂SO₄(aq) stock solutions were analyzed gravimetrically for the sulfate concentration by precipitation as BaSO₄(s).

^c These five Li₂SO₄(aq) stock solutions were analyzed for the lithium concentration with cation-exchange chromatography followed by mass titration of the eluted H⁺ with NaOH(aq).

^d This result is from two separate gravimetric analyses as BaSO₄(s), yielding an average of $m(\text{Li}_2\text{SO}_4) = 0.95864 \pm 0.00009 \text{ mol}\cdot\text{kg}^{-1}$. Two later analyses by cation exchange followed by mass titration of the eluted H⁺ yielded an average of $m(\text{Li}_2\text{SO}_4) = 0.9583 \pm 0.0001 \text{ mol}\cdot\text{kg}^{-1}$.

Table 2 Isopiestic molalities of the NaCl(aq) reference standard, $m(\text{NaCl})$, and of $\text{Li}_2\text{SO}_4(\text{aq})$, $m(\text{Li}_2\text{SO}_4)$, and the corresponding osmotic coefficients $\phi(\text{NaCl})$ and $\phi(\text{Li}_2\text{SO}_4)$, at 298.15 K

$m(\text{NaCl})/\text{mol}\cdot\text{kg}^{-1}$	$\phi(\text{NaCl})^a$	$m(\text{Li}_2\text{SO}_4)/\text{mol}\cdot\text{kg}^{-1}$	$\phi(\text{Li}_2\text{SO}_4)$
Series 1			
1.0457 ± 0.0001	0.9390	0.83052 ± 0.00060	0.7882
1.0286 ± 0.0003	0.9383	0.81702 ± 0.00020	0.7875
0.9500 ± 0.0000	0.9352	0.75354 ± 0.00017	0.7860
0.8672 ± 0.0004	0.9321	0.68658 ± 0.00014	0.7849
0.7686 ± 0.0003	0.9287	0.60733 ± 0.00050	0.7836
0.6828 ± 0.0004	0.9261	0.53833 ± 0.00010	0.7831
0.3776 ± 0.0003	0.9205	0.29595 ± 0.00007	0.7830
0.2731 ± 0.0001	0.9212	0.21228 ± 0.00014	0.7901
Series 2			
0.6304 ± 0.0004	0.9247	0.49833 ± 0.00020	0.7798
0.6150 ± 0.0004	0.9243	0.48558 ± 0.00018	0.7804
0.5942 ± 0.0001	0.9238	0.46910 ± 0.00004	0.7801
0.4630 ± 0.0001	0.9213	0.36374 ± 0.00001	0.7818
0.3913 ± 0.0003	0.9206	0.30607 ± 0.00010	0.7846
Series 3			
3.3794 ± 0.0010	1.0742	2.57735 ± 0.00109	0.9390
3.2480 ± 0.0001	1.0653	2.48425 ± 0.00126	0.9285
2.4919 ± 0.0003	1.0162	1.94278 ± 0.00059	0.8689
1.9843 ± 0.0005	0.9860	1.56533 ± 0.00056	0.8332
1.6418 ± 0.0009	0.9672	1.30464 ± 0.00024	0.8115
1.5937 ± 0.0019	0.9647	1.26715 ± 0.00173	0.8089
1.2454 ± 0.0004	0.9477	0.99407 ± 0.00019	0.7916
1.2080 ± 0.0010	0.9460	0.96522 ± 0.00086	0.7893
1.0843 ± 0.0001	0.9406	0.86693 ± 0.00023	0.7843
Series 4			
1.3439 ± 0.0056	0.9523	1.11759 ± 0.00458	0.7634 ($w = 0$)
1.3167 ± 0.0001	0.9510	1.09603 ± 0.00031	0.7617 ($w = 0$)

Series 5			
2.4151 ± 0.0001	1.0114	1.89333 ± 0.00024	0.8601
2.4143 ± 0.0003	1.0114		0.8598
1.7736 ± 0.0002	0.9743	1.41017 ± 0.00019	0.8169
1.7729 ± 0.0002	0.9742		0.8165
1.1943 ± 0.0004	0.9454	0.95712 ± 0.00003	0.7865
1.1937 ± 0.0009	0.9454		0.7860
1.1854 ± 0.0005	0.9450	0.95183 ± 0.00035	0.7846
1.1856 ± 0.0001	0.9450		0.7847
Series 6			
3.7110 ± 0.0003	1.0972	2.81904 ± 0.00079	0.9629
3.6820 ± 0.0024	1.0952	2.79853 ± 0.00133	0.9606
3.5271 ± 0.0025	1.0844	2.69070 ± 0.00130	0.9476
3.1782 ± 0.0023	1.0606	2.44503 ± 0.00113	0.9190
2.9130 ± 0.0003	1.0430	2.25580 ± 0.00028	0.8979
2.7324 ± 0.0012	1.0313	2.12548 ± 0.00075	0.8839
2.0315 ± 0.0009	0.9887	1.60666 ± 0.00042	0.8334
1.4164 ± 0.0004	0.9558	1.13251 ± 0.00022	0.7969
1.0872 ± 0.0004	0.9408	0.87164 ± 0.00036	0.7823
0.8836 ± 0.0002	0.9327	0.70808 ± 0.00012	0.7759
Series 7			
1.2399 ± 0.0010	0.9475	0.99337 ± 0.00088	0.7884
0.8279 ± 0.0003	0.9307	0.66321 ± 0.00045	0.7746
0.7054 ± 0.0001	0.9268	0.56415 ± 0.00006	0.7725
0.6407 ± 0.0002	0.9249	0.51163 ± 0.00017	0.7722
0.5176 ± 0.0002	0.9221	0.41226 ± 0.00026	0.7718
0.4231 ± 0.0007	0.9208	0.33535 ± 0.00041	0.7745
0.4177 ± 0.0001	0.9208	0.33099 ± 0.00013	0.7746
0.3048 ± 0.0005	0.9207	0.23968 ± 0.00041	0.7806 ($w = 0$)
0.2931 ± 0.0004	0.9209	0.23022 ± 0.00005	0.7816
0.2876 ± 0.0005	0.9209	0.22709 ± 0.00021	0.7775
0.2561 ± 0.0001	0.9215	0.20030 ± 0.00020	0.7855

0.2520 ± 0.0004	0.9216	0.19711 ± 0.00032	0.7855
0.2101 ± 0.0004	0.9230	0.16344 ± 0.00025	0.7910
0.2004 ± 0.0004	0.9234 ₅	0.15565 ± 0.00028	0.7926
Series 8			
0.2959 ± 0.0005	0.9208	0.23205 ± 0.00014	0.7828
0.2500 ± 0.0004	0.9217	0.19538 ± 0.00014	0.7862
0.2300 ± 0.0003	0.9223	0.17942 ± 0.00011	0.7882
0.2021 ± 0.0003	0.9234	0.15717 ± 0.00019	0.7916
0.1395 ± 0.0001	0.9275	0.10698 ± 0.00025	0.8063
0.1394 ± 0.0002	0.9275	0.10688 ± 0.00004	0.8065
Series 10			
0.5046 ± 0.0001	0.9219	0.40111 ± 0.00016	0.7732
0.4945 ± 0.0004	0.9217	0.39234 ± 0.00007	0.7745
Series 13			
0.6316 ± 0.0016	0.9247	0.51121 ± 0.00322	0.7616 ($w = 0$)
		0.51199 ± 0.00289	0.7605 ($w = 0$)
0.6185 ± 0.0001	0.9244	0.49390 ± 0.00007	0.7717
		0.49445 ± 0.00004	0.7709

^a Osmotic coefficients for the NaCl(aq) reference standards were calculated using the equations and parameters reported by Archer [7]. Points given zero weight in the ion-interaction model parameter evaluations are denoted with ($w = 0$).

Table 3 Isopiestic molalities of the NaCl(aq) reference standard, $m(\text{NaCl})$, and of $\text{Li}_2\text{SO}_4(\text{aq})$, $m(\text{Li}_2\text{SO}_4)$, and the corresponding osmotic coefficients $\phi(\text{NaCl})$ and $\phi(\text{Li}_2\text{SO}_4)$, at 323.15 K

$m(\text{NaCl})/\text{mol}\cdot\text{kg}^{-1}$	$\phi(\text{NaCl})^a$	$m(\text{Li}_2\text{SO}_4)/\text{mol}\cdot\text{kg}^{-1}$	$\phi(\text{Li}_2\text{SO}_4)$
Series 4			
1.2809 ± 0.0009	0.9572	1.09604 ± 0.00103	0.7458 ($w = 0$)
1.2019 ± 0.0007	0.9531	1.02630 ± 0.00108	0.7441 ($w = 0$)
1.1080 ± 0.0006	0.9483	0.94349 ± 0.00087	0.7425 ($w = 0$)
1.1079 ± 0.0006	0.9483	0.94342 ± 0.00089	0.7424 ($w = 0$)
0.5222 ± 0.0003	0.9240	0.43031 ± 0.00011	0.7476 ($w = 0$)
0.5186 ± 0.0014	0.9239	0.42624 ± 0.00011	0.7494 ($w = 0$)
Series 8			
0.1981 ± 0.0005	0.9222	0.15548 ± 0.00020	0.7833
0.1477 ± 0.0003	0.9250	0.11480 ± 0.00026	0.7934
Series 9			
3.4603 ± 0.0043	1.0913	2.79692 ± 0.00225	0.9001
3.1761 ± 0.0013	1.0725	2.57910 ± 0.00033	0.8805
3.1708 ± 0.0021	1.0721 ₅	2.57503 ± 0.00069	0.8801
2.3692 ± 0.0016	1.0206	1.94647 ± 0.00059	0.8282
2.3161 ± 0.0036	1.0173	1.90305 ± 0.00112	0.8254
1.4687 ± 0.0005	0.9673	1.21436 ± 0.00075	0.7799
1.4467 ± 0.0031	0.9661	1.19438 ± 0.00183	0.7801
1.4075 ± 0.0023	0.9639	1.16333 ± 0.00102	0.7775
1.3760 ± 0.0020	0.9622	1.13737 ± 0.00082	0.7761
Series 9A			
3.1578 ± 0.0015	1.0713	2.56462 ± 0.00058	0.8794
2.9852 ± 0.0023	1.0600	2.43176 ± 0.00048	0.8675
2.7751 ± 0.0024	1.0464	2.26713 ± 0.00074	0.8539
2.4414 ± 0.0010	1.0251	2.00387 ± 0.00040	0.8326
2.3322 ± 0.0049	1.0183	1.91442 ± 0.00098	0.8270
2.2597 ± 0.0008	1.0138	1.85891 ± 0.00019	0.8216

1.9897 ± 0.0009	0.9973	1.64146 ± 0.00022	0.8059
1.7695 ± 0.0006	0.9843	1.46208 ± 0.00005	0.7942
1.6461 ± 0.0004	0.9772	1.36084 ± 0.00013	0.7880
1.4902 ± 0.0000	0.9685	1.23216 ± 0.00002	0.7809
1.3349 ± 0.0000	0.9600	1.10141 ± 0.00071	0.7757
1.1763 ± 0.0005	0.9518	0.97075 ± 0.00034	0.7689
1.0740 ± 0.0003	0.9467	0.88498 ± 0.00016	0.7659
1.0532 ± 0.0016	0.9456	0.86790 ± 0.00415	0.7650

Series 10

1.1036 ± 0.0004	0.9481	0.91063 ± 0.00033	0.7660
0.9033 ± 0.0003	0.9386	0.74283 ± 0.00010	0.7609
0.7190 ± 0.0002	0.9308	0.58824 ± 0.00014	0.7585
0.5896 ± 0.0003	0.9261	0.47951 ± 0.00003	0.7591
0.4751 ± 0.0006	0.9228	0.38412 ± 0.00003	0.7609

Series 11

0.9010 ± 0.0018	0.9385	0.74311 ± 0.00055	0.7586
0.6667 ± 0.0011	0.9288	0.54561 ± 0.00078	0.7566
0.4959 ± 0.0005	0.9233	0.40234 ± 0.00014	0.7587
0.3691 ± 0.0004	0.9208	0.29663 ± 0.00019	0.7638
0.2775 ± 0.0002	0.9205	0.21996 ± 0.00021	0.7742
0.2653 ± 0.0001	0.9206	0.21051 ± 0.00011	0.7735

Series 12

0.4486 ± 0.0002	0.9221	0.42257 ± 0.00017	0.6526 ($w = 0$)
0.4218 ± 0.0001	0.9216	0.39620 ± 0.00004	0.6541 ($w = 0$)

Series 13

2.1854 ± 0.0002	1.0092	1.80494 ± 0.00047	0.8146
		1.80453 ± 0.00264	0.8148
1.6856 ± 0.0010	0.9795	1.39474 ± 0.00089	0.7892
		1.39510 ± 0.00107	0.7890
1.0187 ± 0.0022	0.9440	0.84021 ± 0.00139	0.7630
		0.84074 ± 0.00068	0.7625
0.6175 ± 0.0002	0.9270	0.50333 ± 0.00030	0.7582

		0.50394 ± 0.00006	0.7573
0.4603 ± 0.0001	0.9224	0.37192 ± 0.00006	0.7611
		0.37208 ± 0.00007	0.7607
0.2429 ± 0.0000	0.9209	0.19187 ± 0.00012	0.7772
		0.19201 ± 0.00010	0.7767

^a Osmotic coefficients for the NaCl(aq) reference standards were calculated using the equations and parameters reported by Archer [7]. Points given zero weight in the ion-interaction model parameter evaluations are denoted with ($w = 0$).

Table 4 Summary by property of available thermodynamic studies yielding the osmotic coefficient, activity coefficient, relative enthalpy, or heat capacity of $\text{Li}_2\text{SO}_4(\text{aq})$

m $\text{mol} \cdot \text{kg}^{-1}$	T K	No. of data points	Property ^a	Relative weight ^b	Reference
0.0731–3.165	298.15	31	ϕ (isopiestic)	1 (2)	Robinson <i>et al.</i> [10]
0.4938–1.8204	298.15	7	ϕ (isopiestic)	0	Majima <i>et al.</i> [11,12]
$m(\text{sat.}) = 3.123$	298.15	1	ϕ (isopiestic)	0	Filippov and Kalinkin [13]
0.6996–3.0403	298.15	17	ϕ (isopiestic)	1	Filippov <i>et al.</i> [14,15]
0.0735–2.6690	298.15	25	ϕ (isopiestic)	n.a.	Baabor <i>et al.</i> [16]
0.0802–2.5658	313.15	20	ϕ (isopiestic)	n.a.	Baabor <i>et al.</i> [17]
0.5401–2.6736	383.14	30	ϕ (isopiestic)	n.a.	Holmes and Mesmer [5]
0.5995–2.5303	413.23	18	ϕ (isopiestic)	n.a.	Holmes and Mesmer [5]
0.5538–2.5981	443.16	14	ϕ (isopiestic)	n.a.	Holmes and Mesmer [5]
0.6617–2.3760	473.17	21	ϕ (isopiestic)	n.a.	Holmes and Mesmer [5]
0.6433–3.1846	498.19	17	ϕ (isopiestic)	n.a.	Holmes and Mesmer [5]
0.1069–2.8190	298.15	64	ϕ (isopiestic)	1 (5)	This study, Table 2
0.1148–2.7969	323.15	56	ϕ (isopiestic)	1 (8)	This study, Table 3
0.1–3.0944	298.15	10	ϕ (v.p.)	0	Pearce and Eckstrom [20]
0.5–3.0	293.15	6	ϕ (v.p.)	n.a.	Kangro and Groeneveld [21]
0.5–3.0	298.15	6	ϕ (v.p.)	0	Kangro and Groeneveld [21]
0.279–1.600	423.15–573.15	28	ϕ (v.p.)	n.a.	Abdulagatov and Azizov [22]
0.1–3.0	298.15	13	ϕ (hyg.)	0	El Guendouzi <i>et al.</i> [23]
$m(\text{sat.})$	298.45–383.50	11	ϕ (v.p.)	n.a.	Applebey <i>et al.</i> [24]
$m(\text{sat.})$	278.15–313.15	8	ϕ (v.p.)	0	Rockland [25]
$m(\text{sat.})$	282.35–322.25	21	ϕ (v.p.)	0	Apleblat and Korin [26]
0.0070–1.0139	268.70–273.11	26	ϕ (f.t.)	n.a.	Indelli [27]
0.025–2.0	298.15	7	Emf	0	Åkerlöf [28]
0.05–2.9	298.15	12	Emf	0	Faverio <i>et al.</i> [29]
0.1–3.0	298.15	14	Emf(t_+)	n.a.	Mussini <i>et al.</i> [31]
	308.15		Emf(t_+)	n.a.	Sircar <i>et al.</i> [32]
0.00016–0.1 ^c	298.15	38	$\Delta_{\text{dil}}H_{\text{m}}$	2	Lange and Streeck [34]
0.0914–3.000	298.15	19	$\Delta_{\text{dil}}H_{\text{m}}$	1 (3)	Thompson <i>et al.</i> [35]
0.278–3.08	298.15	8	$\Delta_{\text{dil}}H_{\text{m}}$	1	Solov'eva <i>et al.</i> [36]
0.08–3.00	283.15	15	$\Delta_{\text{dil}}H_{\text{m}}$	n.a.	Frolov <i>et al.</i> [37]
0.05–2.99	298.15	26	$\Delta_{\text{dil}}H_{\text{m}}$	0.5 (8)	Frolov <i>et al.</i> [37]
0.20–2.99	313.15	16	$\Delta_{\text{dil}}H_{\text{m}}$	n.a.	Frolov <i>et al.</i> [37]

0.1728–0.9186	303.15	10	$\Delta_{\text{dil}}H_{\text{m}}$	n.a.	Leung and Millero [38]
0.0623–0.9409	298.15	11	c_p	0	Apelblat [39]

^a Property: ϕ (isopiestic) denotes osmotic coefficients calculated from isopiestic equilibrium molalities, ϕ (v.p.) denotes osmotic coefficients calculated from non-isopiestic vapor pressure measurements, ϕ (hyg.) denotes osmotic coefficients determined by the hygrometric method, Emf denotes Emf measurements with cell A or cell B that can be used to derive values of γ_{\pm} , Emf(t_+) denotes Emf measurements for a concentration cell with transference, $\Delta_{\text{dil}}H_{\text{m}}$ denotes enthalpies of dilution, and c_p denotes heat capacities per gram of solution measured at constant pressure.

^b These are the relative weights assigned for an individual property: ϕ , $\ln \gamma_{\pm}$, $\Delta_{\text{dil}}H_{\text{m}}$, or $C_{p,\phi}$. The notation n.a. identifies studies that were not analyzed for reasons discussed in the text. Numbers given in parentheses are the number of data points given zero weight in the evaluation of the parameters reported in Table 5 for the two ion-interaction models. The rejected osmotic coefficients from the study of Robinson *et al.* [10] are those for the lowest two molalities of $m = 0.07310$ and $0.08635 \text{ mol}\cdot\text{kg}^{-1}$, and for the present study are identified in Tables 2 and 3. The three rejected enthalpies of dilution from the study of Thompson *et al.* [35] are those that they also rejected in their least-squares fit, and for the study of Frolov *et al.* [37] are for the five experiments with final molalities ranging from $m = 2.83$ to $2.21 \text{ mol}\cdot\text{kg}^{-1}$ and the four experiments with final molalities from $m = 0.15$ to $0.05 \text{ mol}\cdot\text{kg}^{-1}$.

^c The concentrations are reported in molarity units, $\text{mol}\cdot\text{L}^{-1}$, for the studies of Lange and Streeck [34] and Sircar *et al.* [32]. For all of the other studies the concentrations are reported in molality units, $\text{mol}\cdot\text{kg}^{-1}$.

Table 5 Parameters and standard errors for the ion-interaction model applied to $\text{Li}_2\text{SO}_4(\text{aq})$ and Debye-Hückel limiting law slopes, at temperatures of 298.15 and 323.15 K

Parameter	Parameter value ^a at $T =$ 298.15 K	Parameter value ^a at $T =$ 323.15 K
$\beta^{(0)}(\text{Li}, \text{SO}_4)/\text{kg}\cdot\text{mol}^{-1}$	0.121177 (0.0042)	0.128034 (0.0021)
$\beta^{(1)}(\text{Li}, \text{SO}_4)/\text{kg}\cdot\text{mol}^{-1}$	1.01345 (0.0061)	1.05148 (0.0027)
$C^{(0)}(\text{Li}, \text{SO}_4)/\text{kg}^2\cdot\text{mol}^{-2}$	-1.9318×10^{-4} (0.2144)	-1.6822×10^{-3} (0.0139)
$C^{(1)}(\text{Li}, \text{SO}_4)/\text{kg}^2\cdot\text{mol}^{-2}$	0.40159 (0.0252)	0.35428 (0.0139)
$\alpha/\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$	2.0	2.0
$\omega/\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$	2.5	2.5
$A\phi/\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$	0.391475	0.410277
$s(\phi)$	0.0030	0.0012
$E^\circ(\text{cell B})/\text{V}$	2.66960 ± 0.00057	
$\left\{ \frac{\partial \beta^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	1.7196×10^{-4} (0.0387)	
$\left\{ \frac{\partial \beta^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	1.6418×10^{-3} (0.0070)	
$\left\{ \frac{\partial C^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg}^2\cdot\text{mol}^{-2}\cdot\text{K}^{-1}$	-5.0022×10^{-5} (0.0126)	
$\left\{ \frac{\partial C^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg}^2\cdot\text{mol}^{-2}\cdot\text{K}^{-1}$	3.5467×10^{-3} (0.0203)	
A_H/RT	0.801844	
$s(\Delta_{\text{dil}}H_m)/\text{kJ}\cdot\text{mol}^{-1}$	0.0295	

^a The number (dimensionless) in parentheses following a coefficient value is the standard error divided by the coefficient value. The maximum molality to which the osmotic/activity model coefficients apply is $m = 3.165 \text{ mol}\cdot\text{kg}^{-1}$ at 298.15 K and $m = 2.7969 \text{ mol}\cdot\text{kg}^{-1}$ at 323.15 K. The quantities $s(\phi)$ and $s(\Delta_{\text{dil}}H_m)$ are the standard deviations to the model fits for ϕ and $\Delta_{\text{dil}}H_m$, respectively. For the standard 3-parameter Ion-interaction model at 298.15 K: $\beta^{(0)}(\text{Li}, \text{SO}_4)/\text{kg}\cdot\text{mol}^{-1} = 0.139395$ (0.0025), $\beta^{(1)}(\text{Li}, \text{SO}_4)/\text{kg}\cdot\text{mol}^{-1} = 1.22395$ (0.0041), $C(\text{Li}, \text{SO}_4)/\text{kg}^2\cdot\text{mol}^{-2} = -1.6078 \times 10^{-3}$

$$\begin{aligned}
(0.0210), s(\phi) = 0.0044, \left\{ \frac{\partial \beta^{(0)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} &= 4.8384 \times 10^{-4} (0.0069), \\
\left\{ \frac{\partial \beta^{(1)}(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} &= 1.5809 \times 10^{-3} (0.0120), \left\{ \frac{\partial C(\text{Li}, \text{SO}_4)}{\partial T} \right\}_p / \text{kg}^2 \cdot \text{mol}^{-2} \cdot \text{K}^{-1} \\
&= -7.8738 \times 10^{-5} (0.0051), \text{ and } s(\Delta_{\text{dil}} H_{\text{m}}) / \text{kJ} \cdot \text{mol}^{-1} = 0.045; \text{ at } 323.15 \text{ K:} \\
\beta^{(0)}(\text{Li}, \text{SO}_4) / \text{kg} \cdot \text{mol}^{-1} &= 0.14594 (0.0017), \beta^{(1)}(\text{Li}, \text{SO}_4) / \text{kg} \cdot \text{mol}^{-1} = 1.22638 (0.0028), \\
C(\text{Li}, \text{SO}_4) / \text{kg}^2 \cdot \text{mol}^{-2} &= -3.1886 \times 10^{-3} (0.0081), \text{ and } s(\phi) = 0.0027.
\end{aligned}$$

Table 6 Smoothed values of the osmotic coefficients ϕ , mean activity coefficients γ_{\pm} , water activities a_w , and relative apparent molar enthalpies L_{ϕ} for $\text{Li}_2\text{SO}_4(\text{aq})$ calculated using the parameters of Table 5 for the four parameter ion-interaction model

$\frac{m}{\text{mol} \cdot \text{kg}^{-1}}$	ϕ	a_w^a	γ_{\pm}	$\frac{L_{\phi}}{\text{J} \cdot \text{mol}^{-1}}$
$T = 298.15 \text{ K}$				
0.01	0.8990	0.9995143	0.7154	893
0.02	0.8720	0.999058	0.6434	1195
0.04	0.8434	0.998178	0.5665	1567
0.06	0.8270	0.997322	0.5212	1814
0.08	0.8160	0.996478	0.4897	2000
0.1	0.8080	0.995643	0.4658	2148
0.2	0.7877	0.991522	0.3966	2617
0.3	0.7798	0.987436	0.3604	2885
0.4	0.7765	0.983353	0.3370	3072
0.5	0.7756	0.97926	0.3203	3220
0.6	0.7764	0.97514	0.3077	3346
0.7	0.7785	0.97098	0.2979	3460
0.8	0.7816	0.96677	0.2902	3568
0.9	0.7857	0.96250	0.2841	3674
1.0	0.7905	0.95818	0.2791	3780
1.2	0.8024	0.94929	0.2722	3994
1.4	0.8167	0.94008	0.2681	4218
1.6	0.8332	0.93048	0.2662	4455
1.8	0.8514	0.92051	0.2661	4707
2.0	0.8711	0.91014	0.2675	4976
2.2	0.8921	0.89936	0.2701	5260
2.4	0.9142	0.88818	0.2738	5563
2.6	0.9372	0.87661	0.2785	5883
2.8	0.9610	0.86465	0.2841	6221
3.0	0.9855	0.85233	0.2906	6578
3.131 ^b	1.0019	0.84405	0.2954	6823

$T = 323.15 \text{ K}$			
0.01	0.8941	0.999517	0.7038
0.02	0.8657	0.999065	0.6296
0.04	0.8354	0.998196	0.5506
0.06	0.8179	0.997351	0.5044
0.08	0.8061	0.996521	0.4722
0.1	0.7975	0.995699	0.4479
0.2	0.7748	0.991660	0.3774
0.3	0.7653	0.987668	0.3405
0.4	0.7607	0.983689	0.3166
0.5	0.7588	0.979704	0.2995
0.6	0.7586	0.97570	0.2865
0.7	0.7598	0.97166	0.2764
0.8	0.7620	0.96759	0.2683
0.9	0.7650	0.96347	0.2617
1.0	0.7688	0.95930	0.2563
1.2	0.7783	0.95078	0.2483
1.4	0.7899	0.94198	0.2430
1.6	0.8031	0.93291	0.2396
1.8	0.8175	0.92355	0.2377
2.0	0.8328	0.91391	0.2369
2.2	0.8488	0.90400	0.2371
2.4	0.8653	0.89383	0.2381
2.6	0.8821	0.88342	0.2397
2.8 ^c	0.8991	0.87279	0.2418

^a The values of a_w are reported to the minimum number of figures necessary to reproduce the tabulated values of ϕ to ≤ 0.0003 below $m = 0.05 \text{ mol}\cdot\text{kg}^{-1}$ and to ≤ 0.0001 at higher molalities.

^b Assessed molality at 298.15 K of a saturated solution in equilibrium with $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{cr})$.

^c The highest investigated molality is $2.7969 \text{ mol}\cdot\text{kg}^{-1}$. Linke [46] reported the composition of a saturated solution at 323.15 K from a published study that yields $m(\text{sat.}) = 2.92 \text{ mol}\cdot\text{kg}^{-1}$. However, this value may be too low because results from several other

studies at nearby temperatures, when interpolated to this temperature, yield $m(\text{sat.}) \approx 3.00 \text{ mol}\cdot\text{kg}^{-1}$ which is probably slightly more accurate.

Figure Captions

Fig. 1 (a) Experimental ϕ values of $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 K (weighted data only) and (b) deviations of experimental values from the four-parameter extended Pitzer model fit using the parameters of Table 5 as a function of the square root of the molality. Plotting symbols: ●, this research (Table 2); ○, Filippov *et al.* [14,15]; □, Robinson *et al.* [10].

Fig. 2 Deviations of rejected (zero-weighted) experimental non-isopiestic values of ϕ of $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 K from the four-parameter extended Pitzer model fit using the parameters of Table 5 as a function of the square root of the molality. Plotting symbols: □, Pearce and Eckstrom [20]; ○, Kangro and Groeneveld [21]; +, Rockland [25]; ●, El Guendouzi *et al.* [23].

Fig. 3 (a) Experimental ϕ values of $\text{Li}_2\text{SO}_4(\text{aq})$ at 323.15 K (weighted data only) and (b) deviations of experimental values from the four-parameter extended Pitzer model fit using the parameters of Table 5 as a function of the square root of the molality. Plotting symbols: ●, this research (Table 3).

Fig. 4 Deviations of the experimental Emf values of $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 K from the four-parameter extended Pitzer model fit using the parameters of Table 5 as a function of the square root of the molality. These Emfs were not used in evaluating the model parameters. Plotting symbols: ●, Faverio *et al.* [29] for cell B; ○, Åkerlöf [28] for cell A.

Fig. 5 (a) Experimental-based relative apparent molar enthalpies L_ϕ values of $\text{Li}_2\text{SO}_4(\text{aq})$ at 298.15 K (weighted data only), where L_ϕ of the final diluted solution were calculated from the four-parameter extended Pitzer model fit using the parameters of Table 5, and (b) deviations of experimental values of $\Delta_{\text{dil}}H_{\text{m}}$ from the model fit as a function of the square root of the molality. Plotting symbols: ●, Frolov *et al.* [37]; +, Solov'eva *et al.* [36]; ○, Thompson *et al.* [35]; ■, Lange and Streeck [34]. All of the points of Frolov *et al.* were based on dilution from the same initial molality of $2.99 \text{ mol}\cdot\text{kg}^{-1}$.

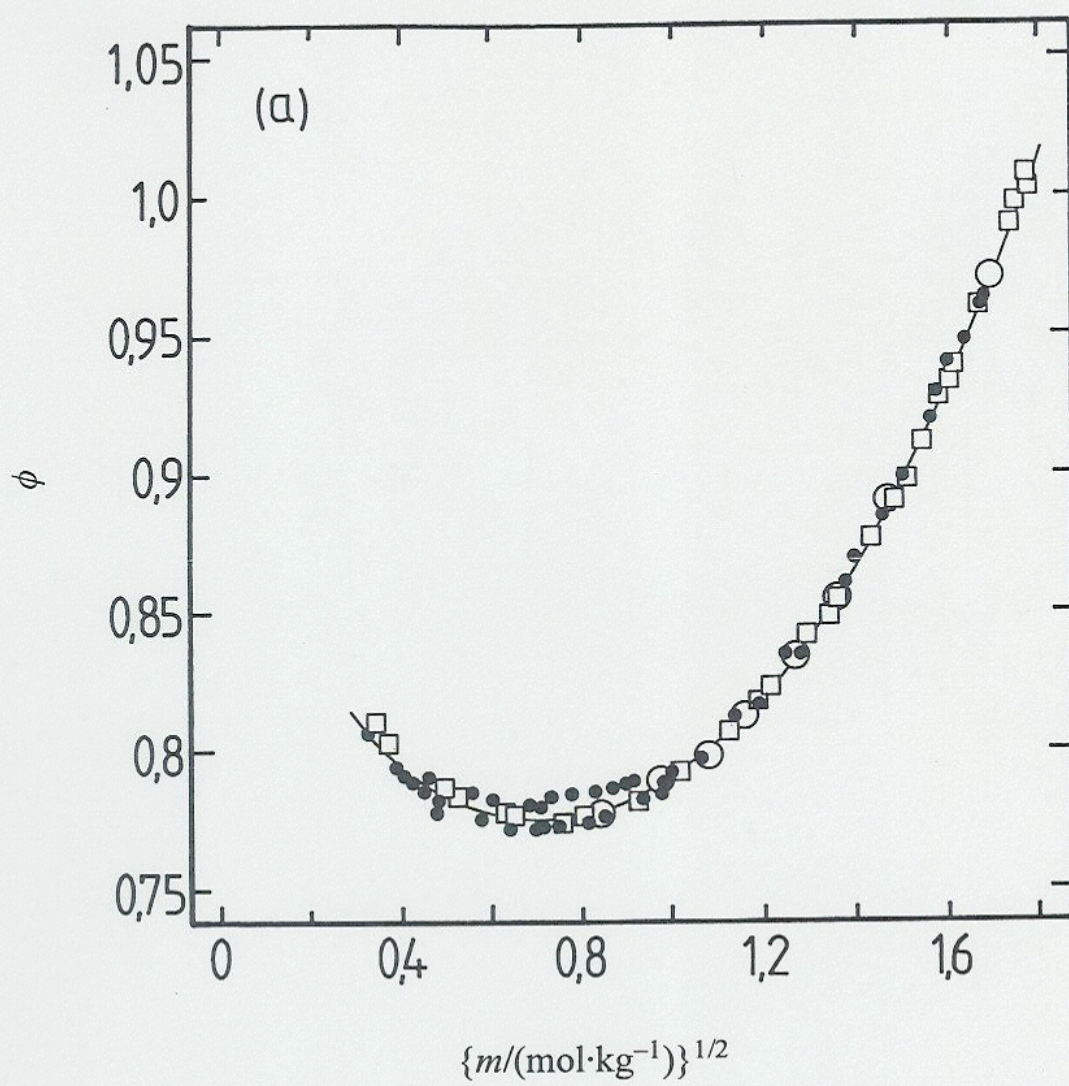


Fig. 1 (a)

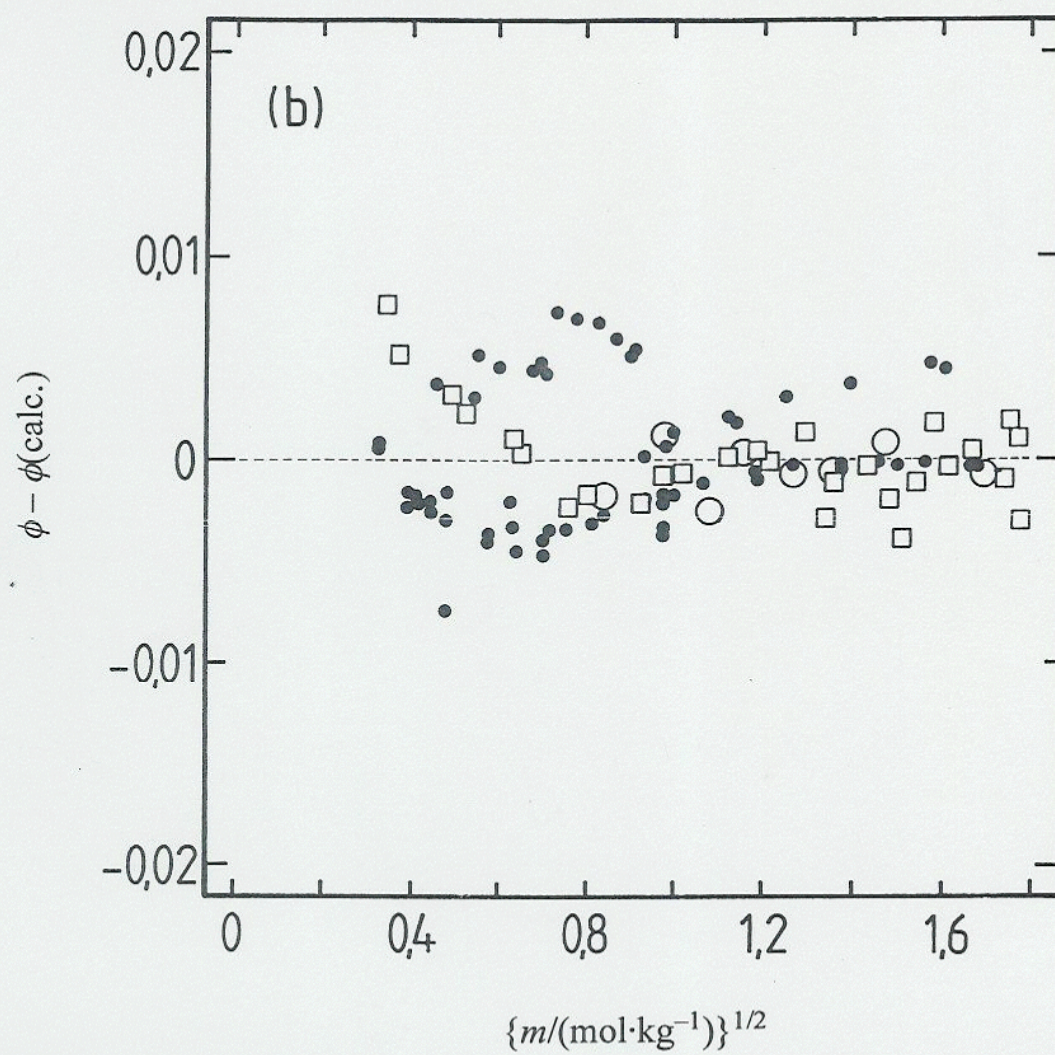


Fig. 1 (b)

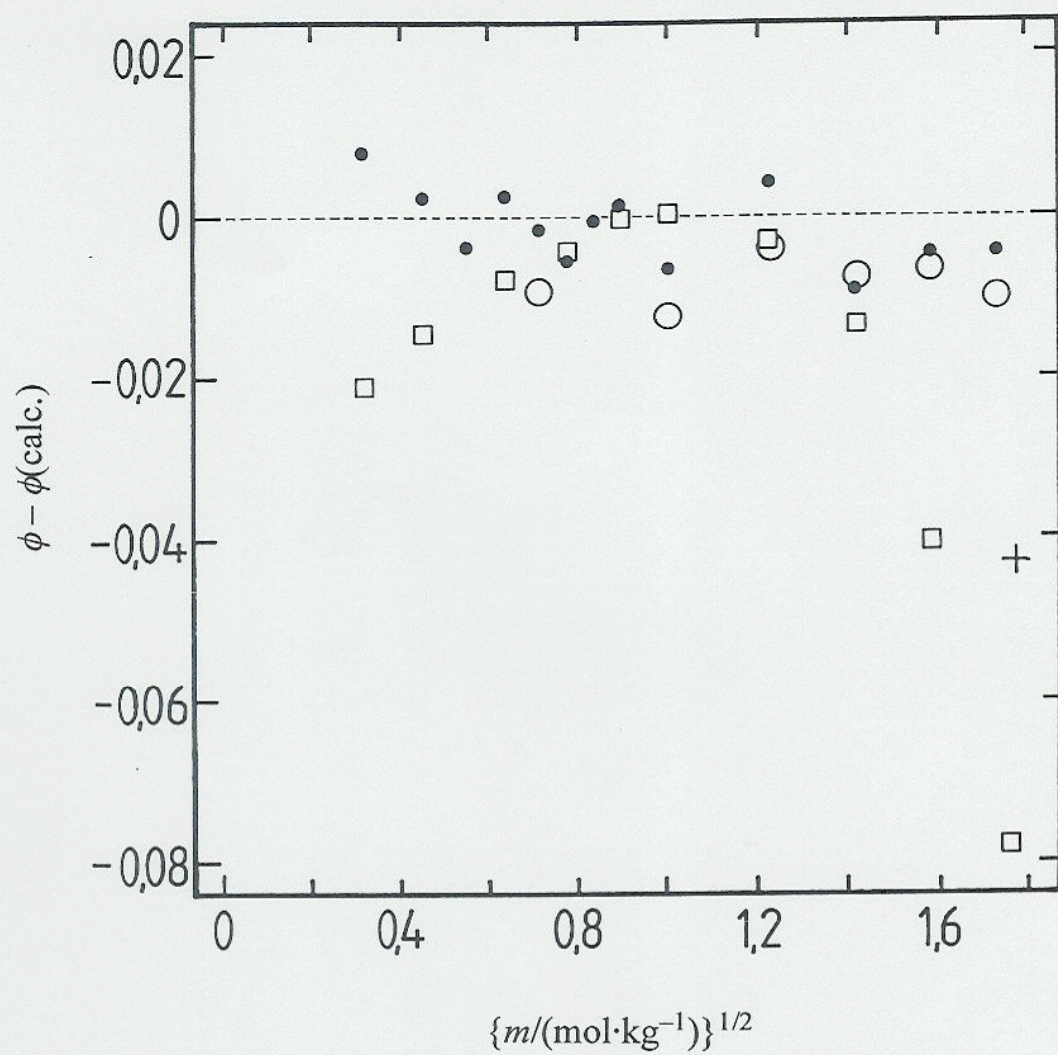


Fig. 2

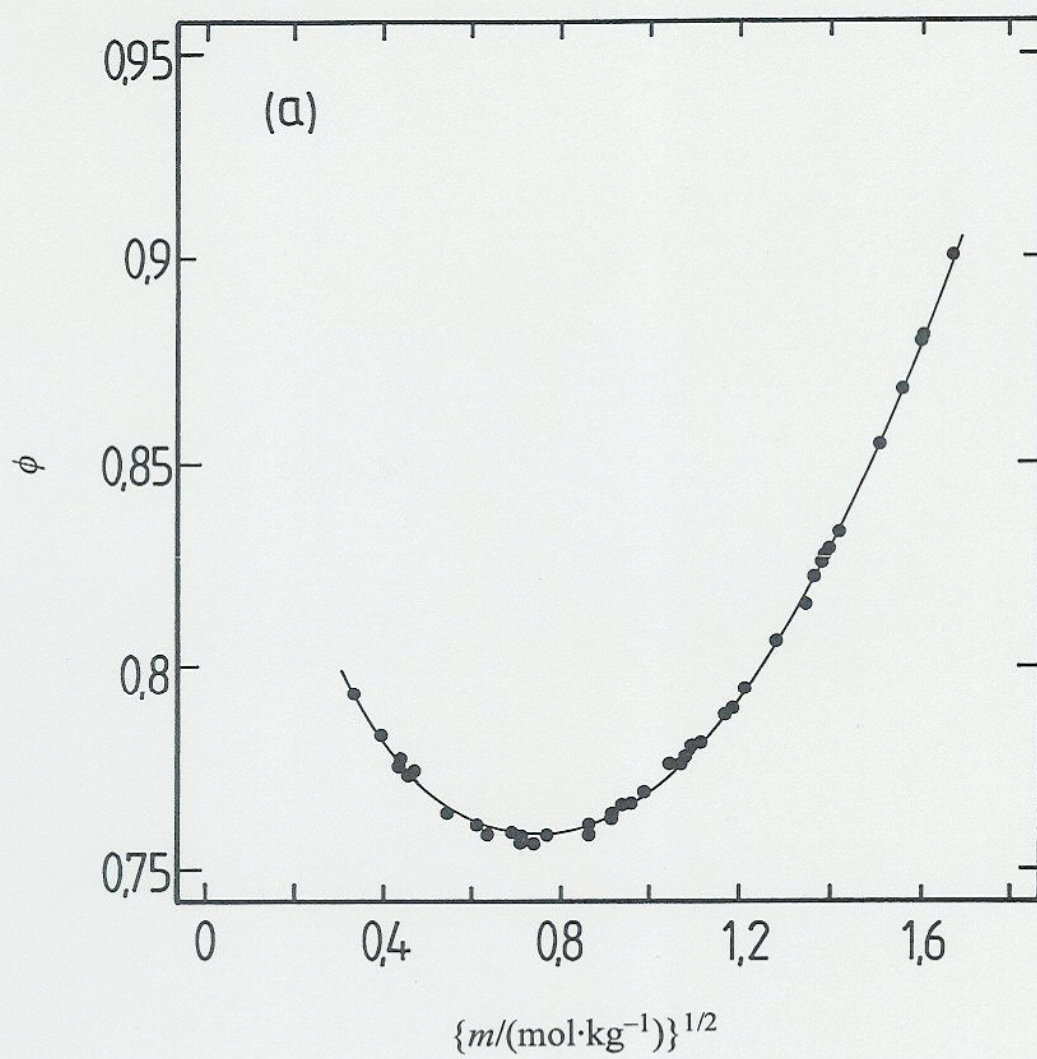


Fig. 3 (a)

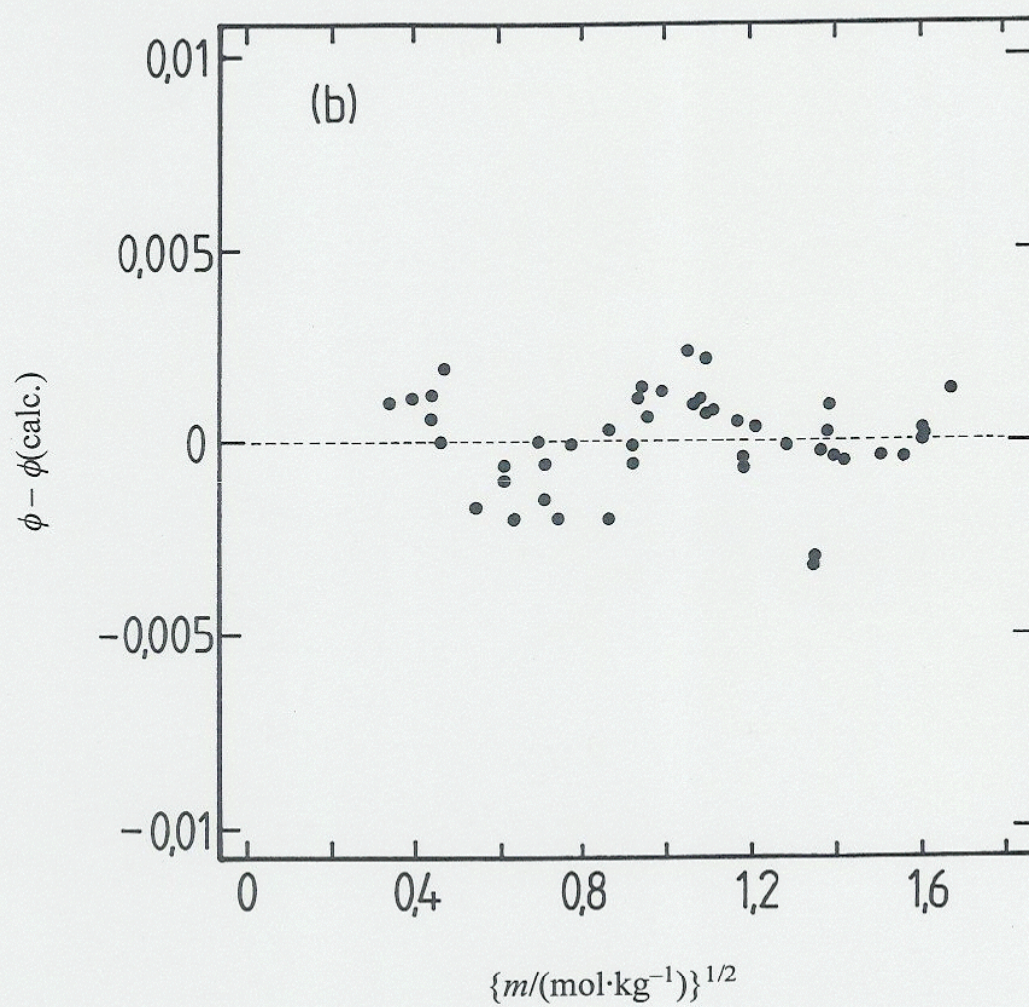


Fig. 3 (b)

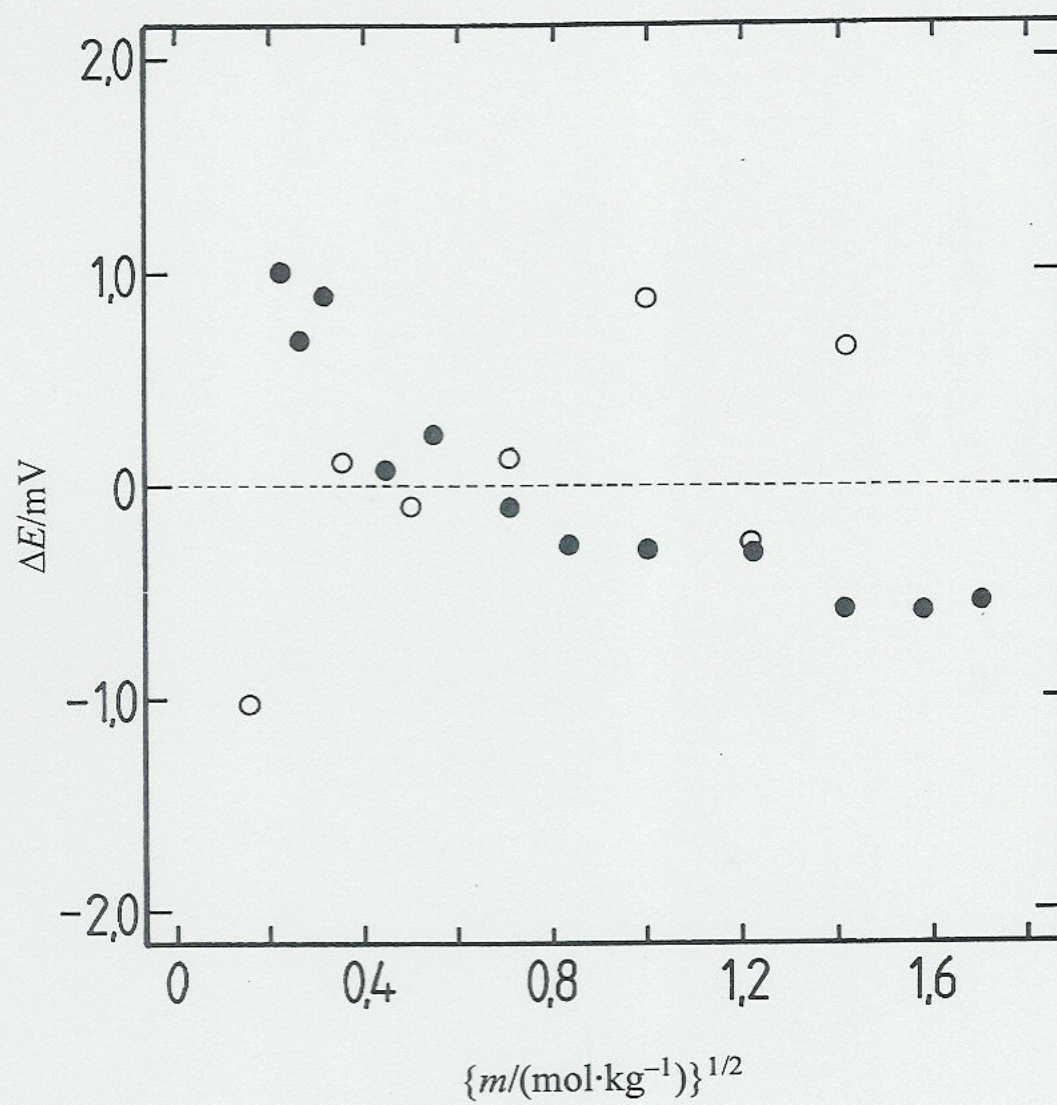


Fig. 4

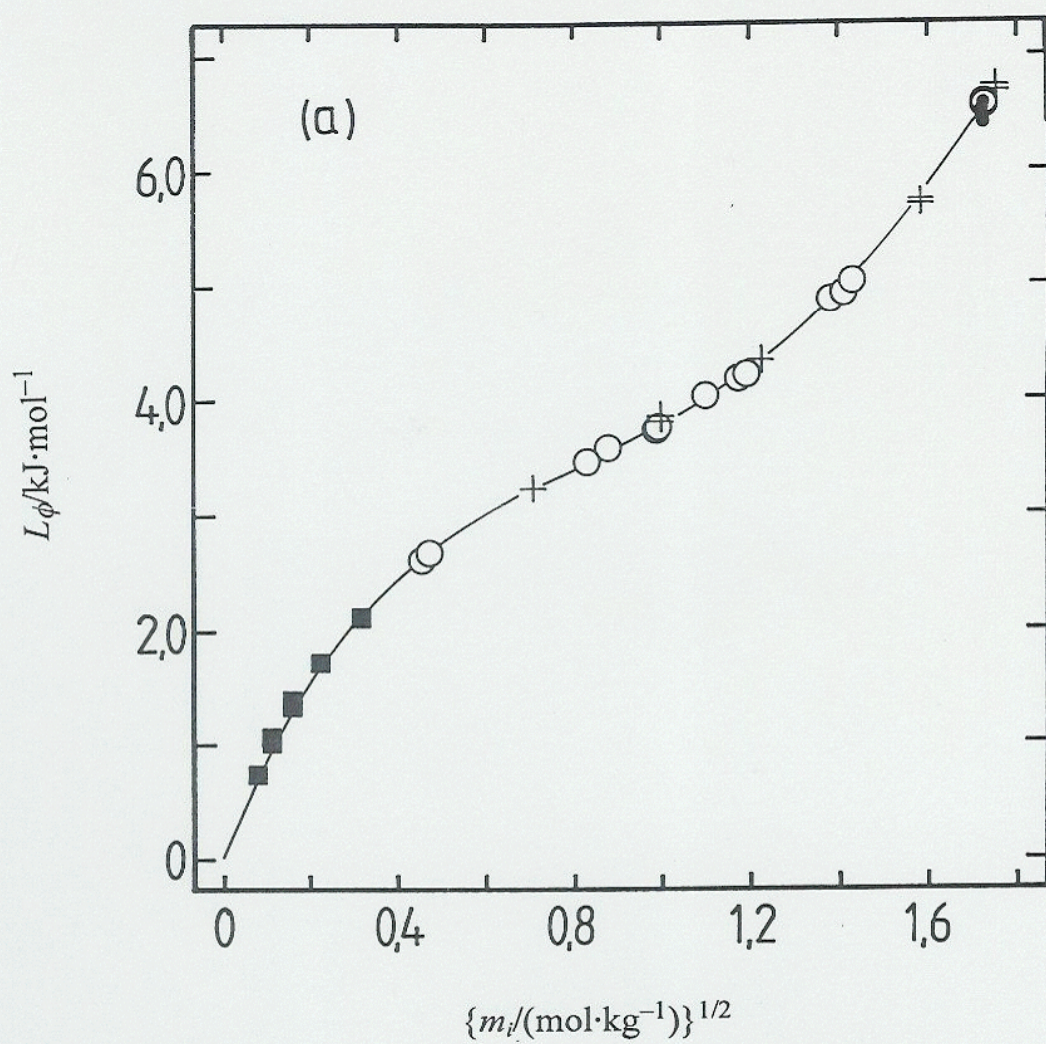


Fig. 5 (a)

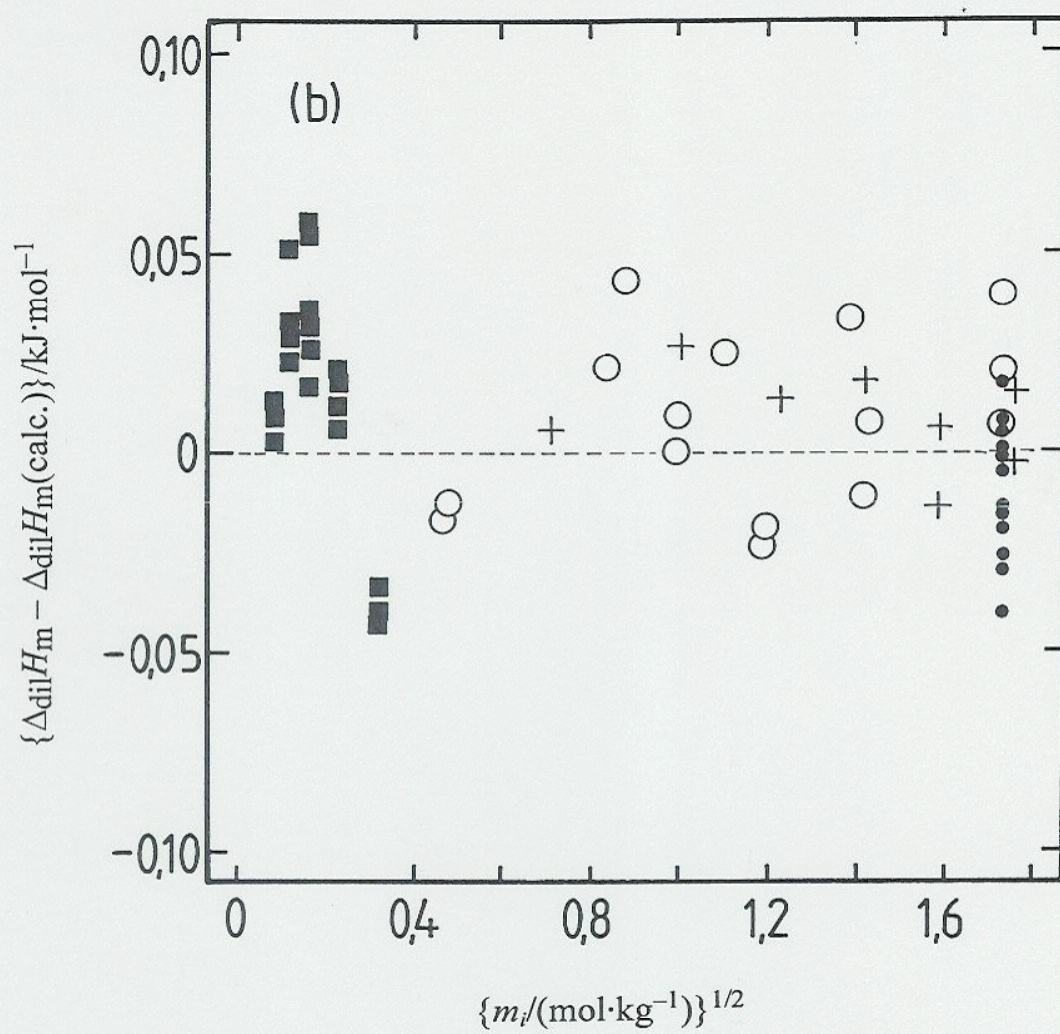


Fig. 5 (b)